Thermoelectric Properties of Self Assemble TiO_2/SnO_2 Nanocomposites

Fred Dynys*, NASA-Glenn, USA;
Ali Sayir, Alp Sehirlioglu, Case Western Reserve University, USA

Recent advances in improving efficiency of thermoelectric materials are linked to nanotechnology. Thermodynamically driven spinodal decomposition was utilized to synthesize bulk nanocomposites. TiO_2/SnO_2 system exhibits a large spinodal region, ranging from 15 to 85 mole % TiO_2. The phase separated microstructures are stable up to 1400 ^oC. Semiconducting TiO_2/SnO_2 powders were synthesized by solid state reaction between TiO_2 and SnO_2. High density samples were fabricated by pressureless sintering. Self assemble nanocomposites were achieved by annealing at 1000 to 1350 ^oC. X-ray diffraction reveal phase separation of $(Ti_xSn_{1-x})O_2$ type phases. The TiO_2/SnO_2 nanocomposites exhibit n-type behavior; a power factor of 70 $\mu W/mK^2$ at 1000 ^oC has been achieved with penta-valent doping. Seebeck, thermal conductivity, electrical resistivity and microstructure will be discussed in relation to composition and doping.

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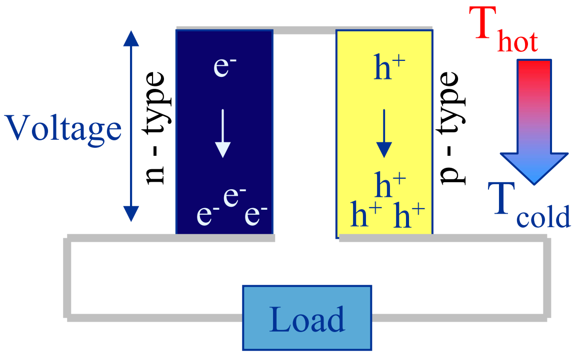
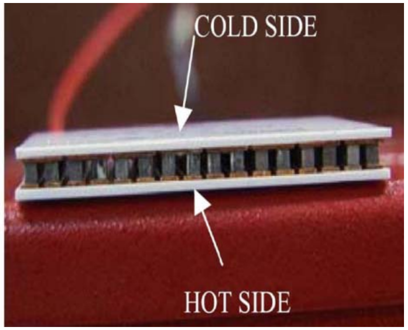
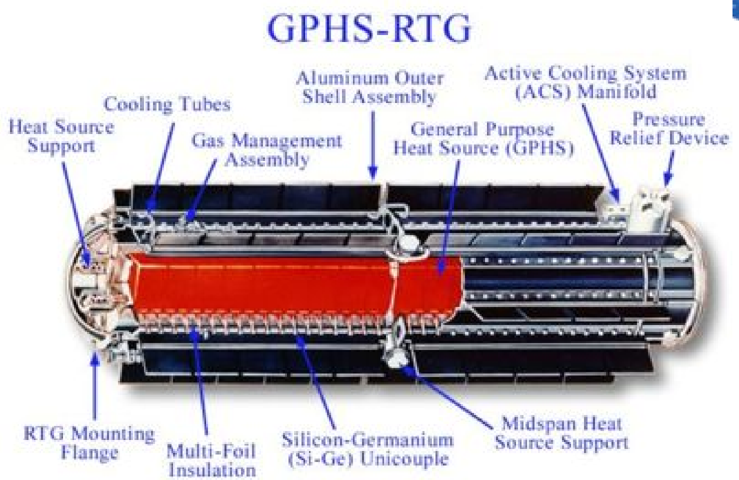
Program Support: NASA Radioisotope Power Systems

Heat to Electric Power Generation



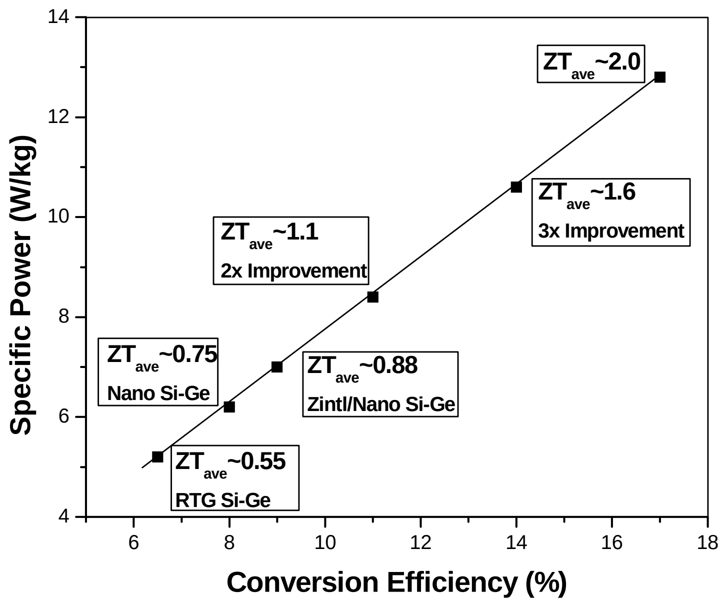




Objective: High Conversion Efficiency

- Reduces Mass, Volume & Cost

Space Power Generation



Waste Heat to Power

- Waste Heat is one of our most under utilized energy resources
- U.S.-energy consumption ~29 tera-kWh (10^{12})
  Barrels of Oil – 170 giga-barrels (10^{9})
- World-energy consumption ~120 tera- kWh (10^{12})
- 20-65 percent is lost in the form of heat
- Maximizes efficiency
- Reduces CO_2 emission

Nanotechnology

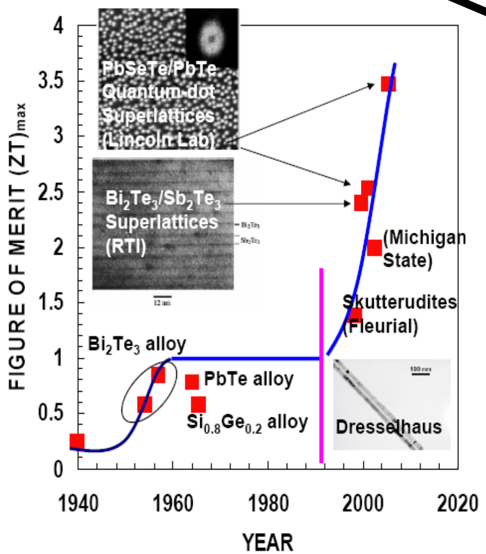
Figure of Merit

$$ZT = \frac{S^2\sigma}{\kappa}T$$

S - Seebeck coefficient
σ – electrical conductivity
κ– thermal conductivity

Efficiency

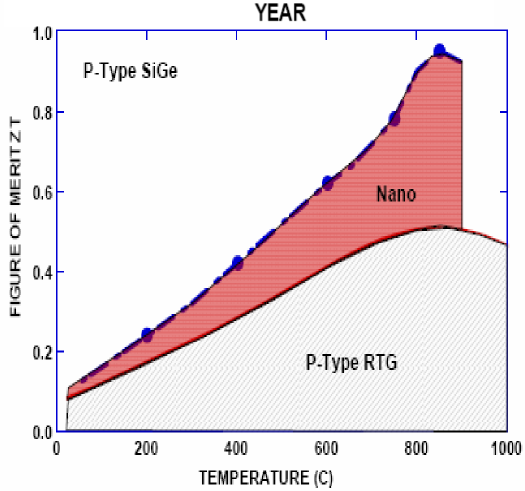
$$\eta_{\max} = \frac{\Delta T}{T_{hot}} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+T_{cold}/T_{hot}}$$

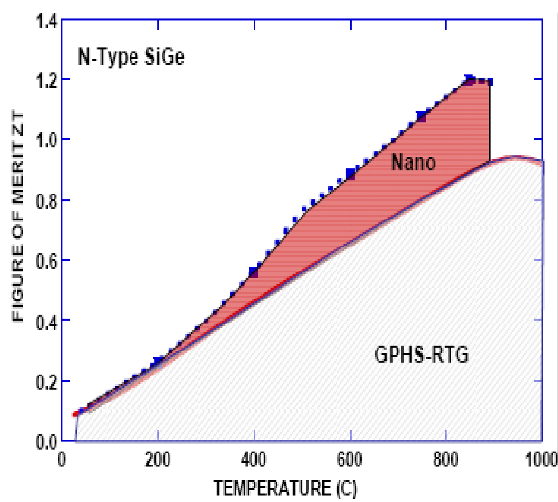


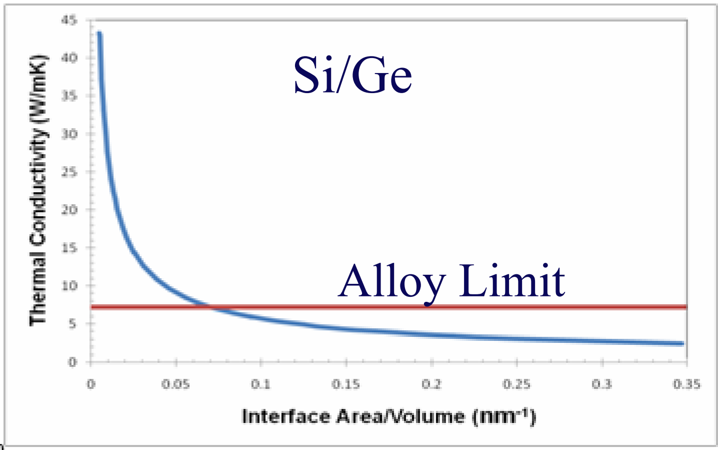
Phonon Scattering:

- Atom disorder
- Alloying
- Anharmonic vibrations
- **Supperlattices**
- **Crystal Structures**
- **Nano-technology**

Fleurial/Chen – JPL/MIT

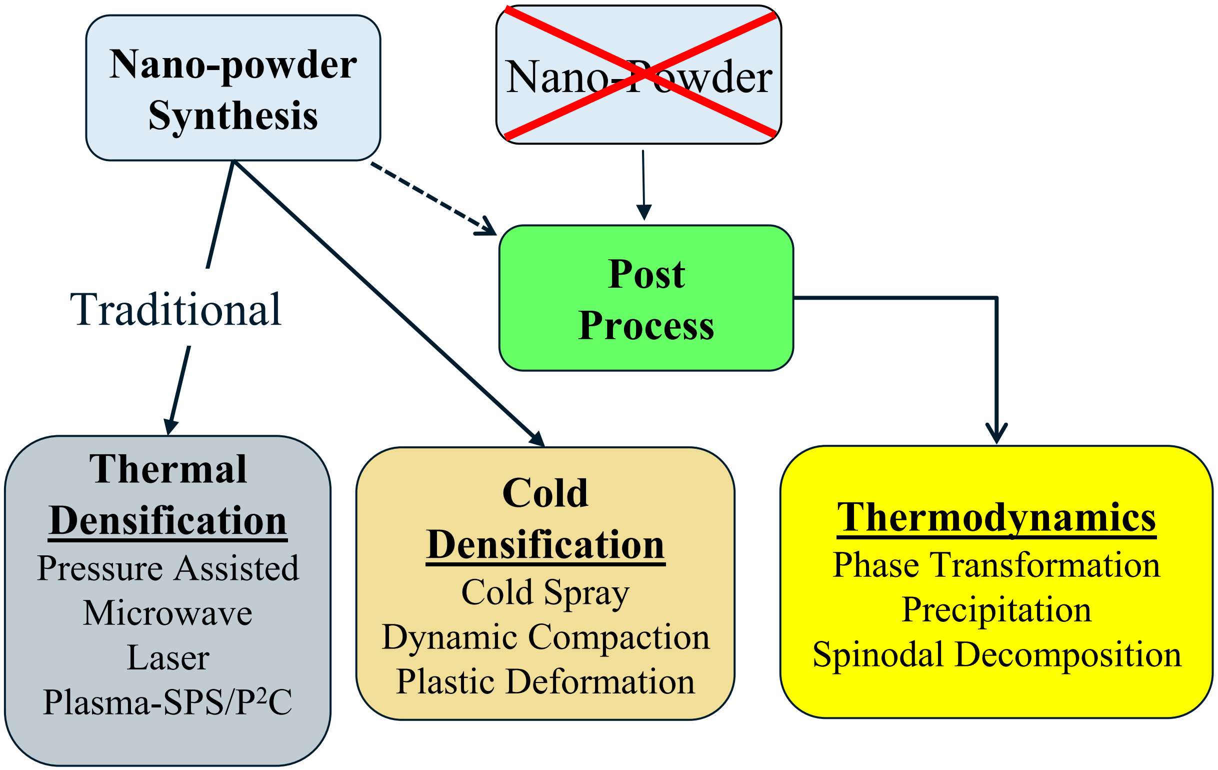






Fabrication of Nanostructure Solids

Goal: Preservation of the nanostructure during fabrication.



Inhibit Grain Growth
- Rapid Thermal Process
- Inclusions
- Lower Temperature

New Approach

Grain Size
- Thermal Aging
- Composition Limited
- Stable

Spinodal Decomposition

$TiO_2 – SnO_2$

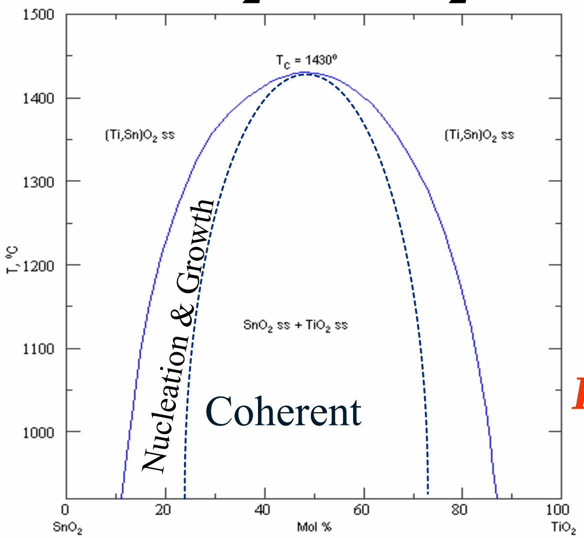


Fig. 10. TEM image of $(Ti_{0.5}/Sn_{0.5})O_2$ ceramics annealed for 48 h.

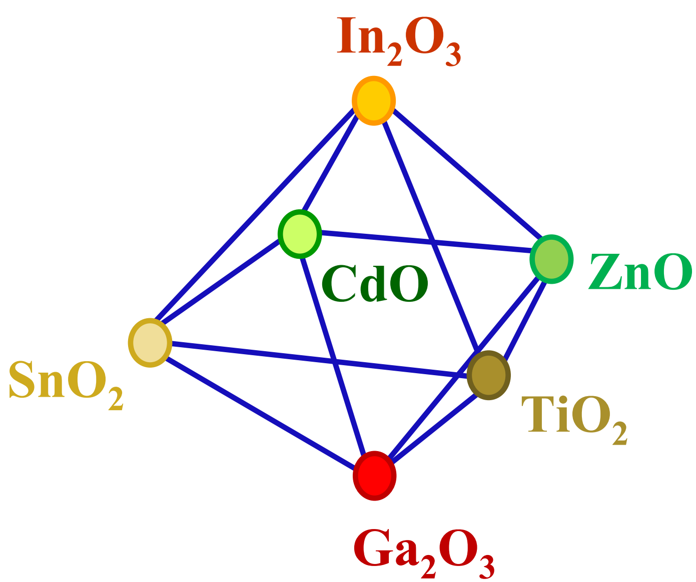
Shultz & Stubican, JACS, 53, 1970

Desired Features
- ~50 nm grains
- High Temperature
- Wide Composition
- Large Δ Mass

Transparent Conducting Oxides

Insulator/Semiconductor/Conductor

- Large Bandgap 2.4-3.8 ev
- N-type –Degenerate Semiconductor



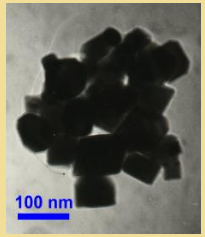
Electrical Conductivity

TCO	σ(S/m) @ RT
ITO	$8x10^5$
In_2O_3	$1x10^6$
SnO_2	$2.5x10^5$
ZnO	$8.3x10^5$
ZnO:Al	$7.7x10^4$
$CdSnO_2$	$7.7x10^5$
CdO:In	$1.7x10^6$

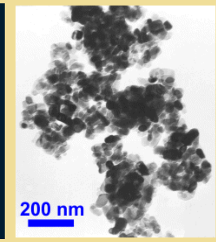
ZnO:Al
ZT~0.6 @ 1000 °C

Experimental

SnO_2
Purity: 99.9%
APS: 50 nm
SSA: 14.2 m^2/g



TiO_2 Rutile
Purity: 99.99 %
APS: 20 nm,
SSA: > 30 m^2/g



Dopants
CoO, MnO_2
Ta_2O_5, In_2O_3

TiO_2/SnO_2
50/50 mol %
75/25 mol %
25/75 mol %

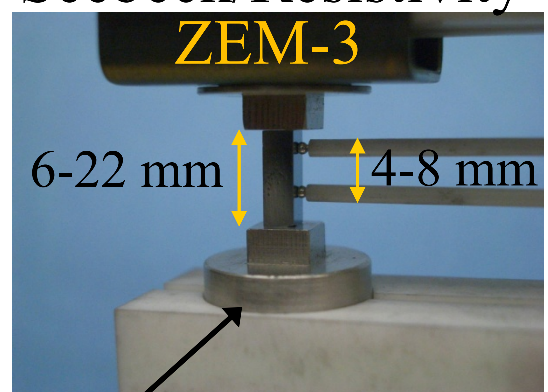
Powder Mixing

Compaction Die Press

Reactive Sintering 1250-1550 °C

Anneal 72 Hrs

Seebeck/Resistivity

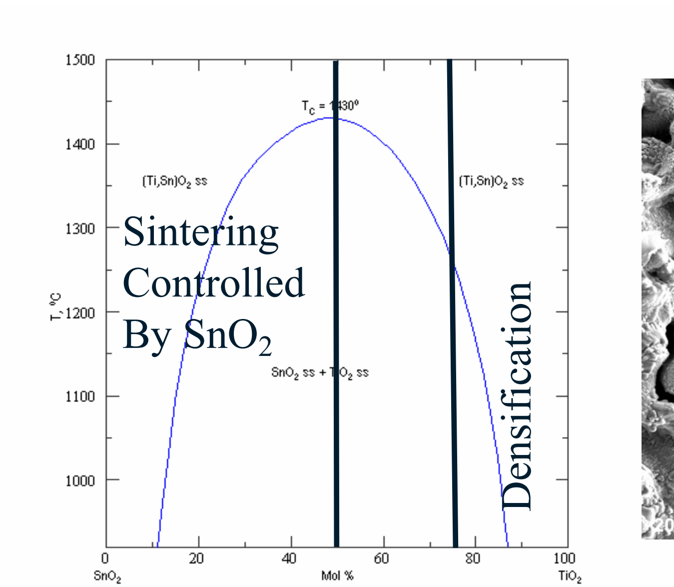


ΔT 0-50 °C/Furnace RT-1000 °C

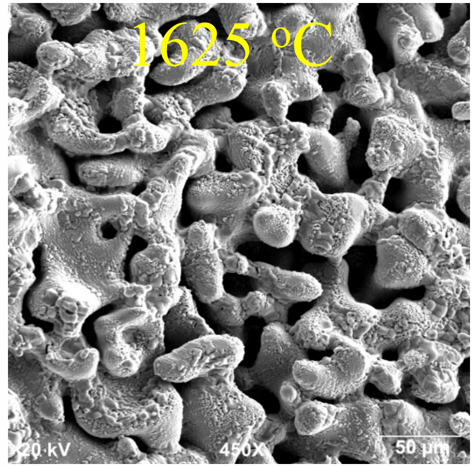
Thermal Conductivity

- **Laser Flash Method- Thermal Diffusivity**
- **Standard**
- **Specific Heat- C_p - Laser Flash**
- **Thermal Conductivity ($K = \alpha\rho C_p$)**

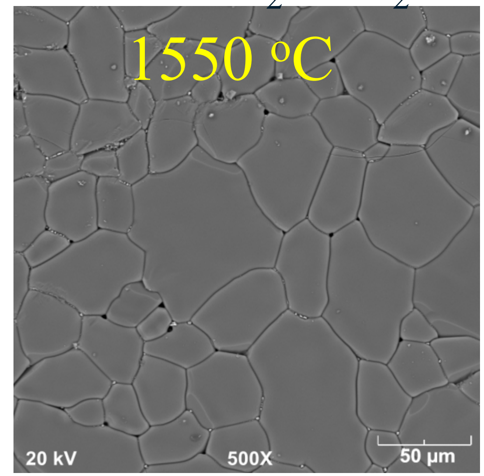
Sintering



50/50 TiO_2/SnO_2



75/25 TiO_2/SnO_2

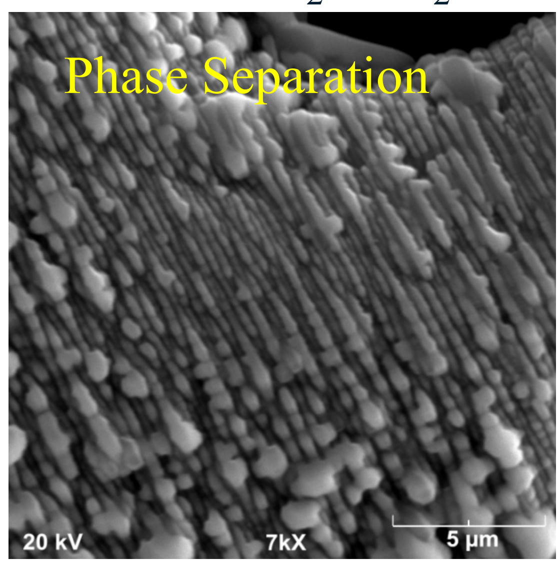


SnO_2 Sintering-Inhibited

- Surface Diffusion <1100 °C
- Evaporation >1100 °C

$SnO_2 \rightarrow SnO + \frac{1}{2}O_{2\,(g)}$

50/50 TiO_2/SnO_2



Ta_2O_5 & In_2O_3 Ineffective Sintering Aids

$$Ta_2O_5 \rightarrow 2Ta^{\bullet}_{Ti,Sn} + 2e' + \tfrac{1}{2}O_2$$

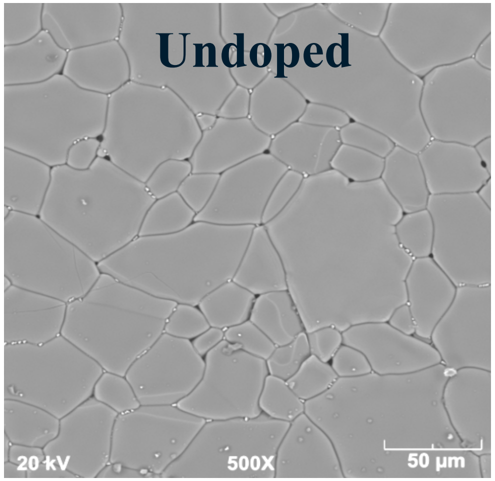
$$In_2O_3 \rightarrow 2In'_{Ti,Sn} + 2V^{\bullet}_O$$

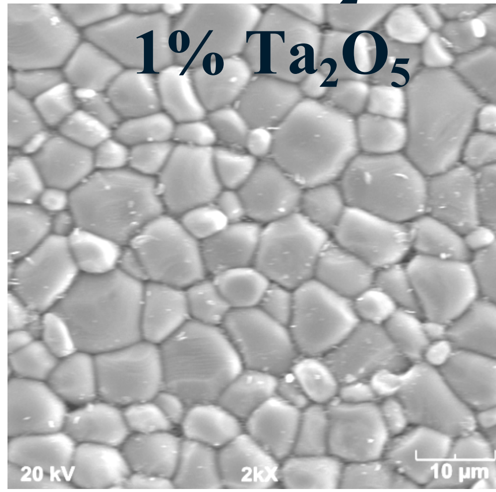
Sintering Aids-SnO_2

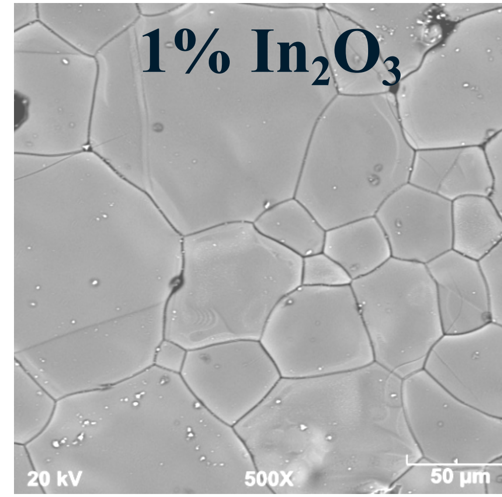
- MnO, CoO, CuO, ZnO

$$CoO \rightarrow Co''_{Ti,Sn} + V^{\bullet\bullet}_O$$

75/25 TiO_2/SnO_2







XRD-Phases (Undoped)

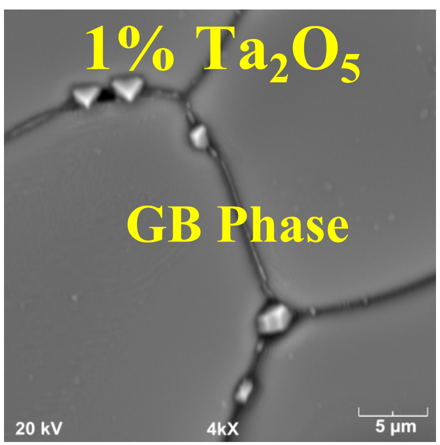
Sintered – $(Ti_{0.8}Sn_{0.2})O_2$
Reduced – TiO_2, Rutile
$(Ti_{0.8}Sn_{0.2})O_2$

XRD-Phases (1% Ta_2O_5)

Sintered – $(Ti_{0.8}Sn_{0.2})O_2$
Annealed – $(Ti_{0.8}Sn_{0.2})O_2$
1250 °C
Reduced – TiO_2, Rutile
$(Ti_{0.8}Sn_{0.2})O_2$

XRD-Phases (1% In_2O_3)

Sintered – TiO_2, Rutile
SnO_2, In_2O_3
Annealed – TiO_2, Rutile
1250 °C SnO_2, In_2O_3



Phase Separation

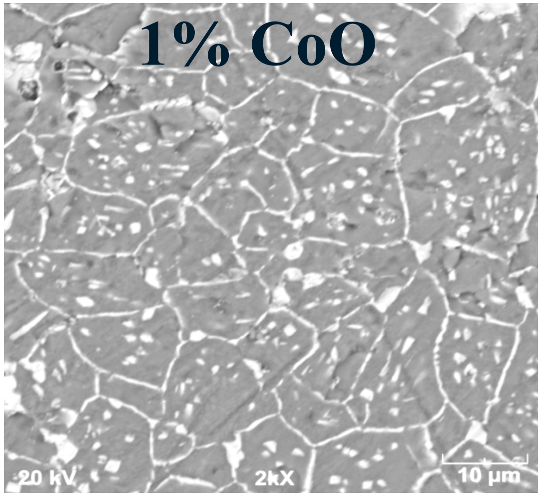
1% CoO XRD

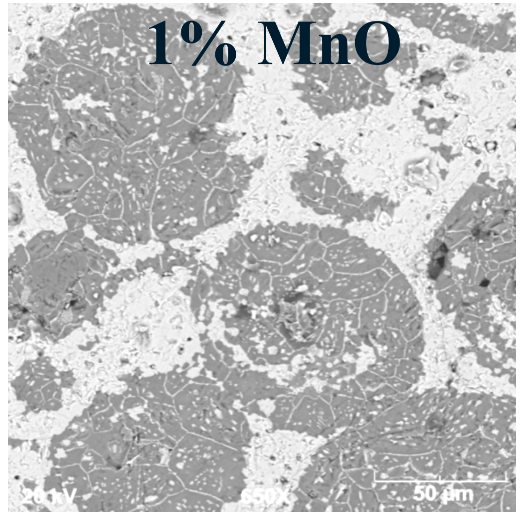
Sintered – $(Ti_{0.8}Sn_{0.2})O_2$
$(Ti_{0.2}Sn_{0.8})O_2$
Annealed – $(Ti_{0.9}Sn_{0.1})O_2$
1000 °C $(Ti_{0.1}Sn_{0.9})O_2$

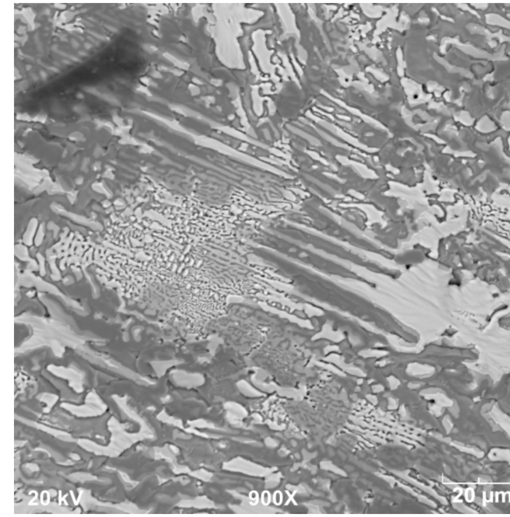
1% MnO XRD

Sintered – $(Ti_{0.8}Sn_{0.2})O_2$
$(Ti_{0.2}Sn_{0.8})O_2$
Annealed – $(Ti_{0.9}Sn_{0.1})O_2$
1000 °C $(Ti_{0.1}Sn_{0.9})O_2$

50/50 TiO_2/SnO_2







XRD-Phases

Sintered – $(Ti_{0.8}Sn_{0.2})O_2$
$(Ti_{0.2}Sn_{0.8})O_{2\backslash}$
TiO_2
Annealed – $(Ti_{0.2}Sn_{0.8})O_2$
1000 °C $(Ti_{0.9}Sn_{0.1})O_2$

XRD-Phases

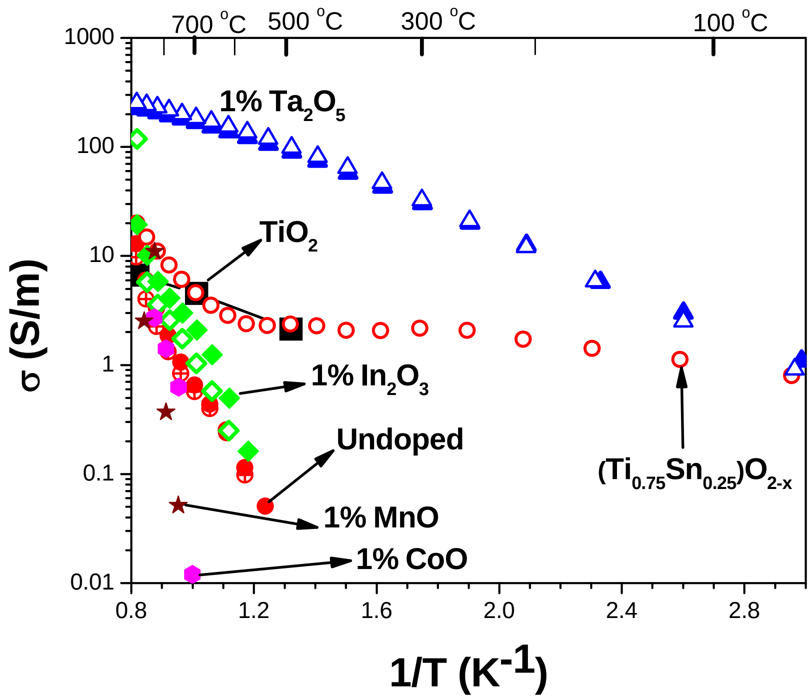
Sintered – $(Ti_{0.8}Sn_{0.2})O_2$
$(Ti_{0.1}Sn_{0.9})O_2$
Annealed – $(Ti_{0.2}Sn_{0.8})O_2$
1000 °C $(Ti_{0.9}Sn_{0.1})O_2$

Microstructure Coarsening @ 1600 °C

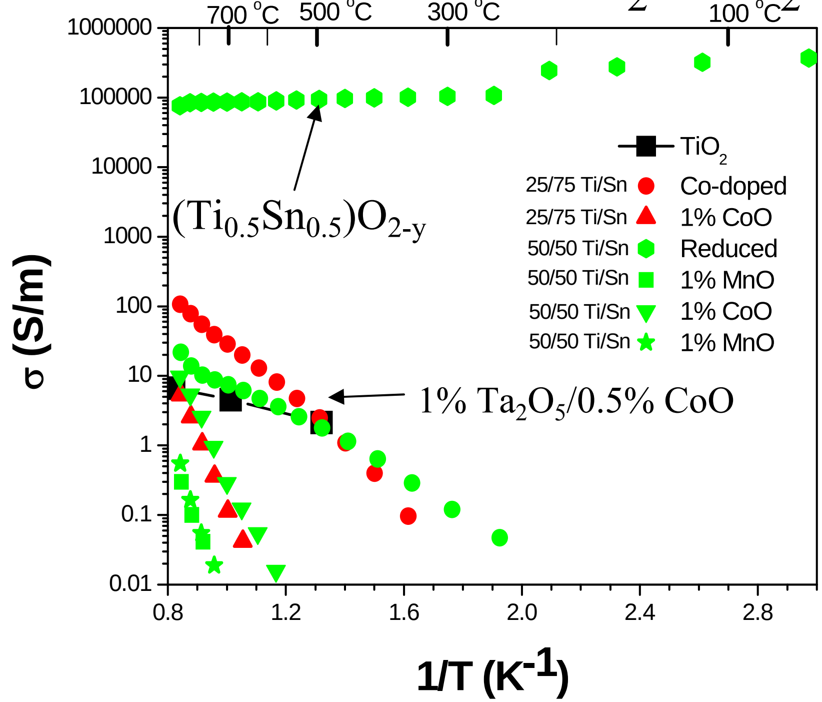
Grain Boundary Phases Segregation

Electrical Conductivity

75/25 TiO_2/SnO_2



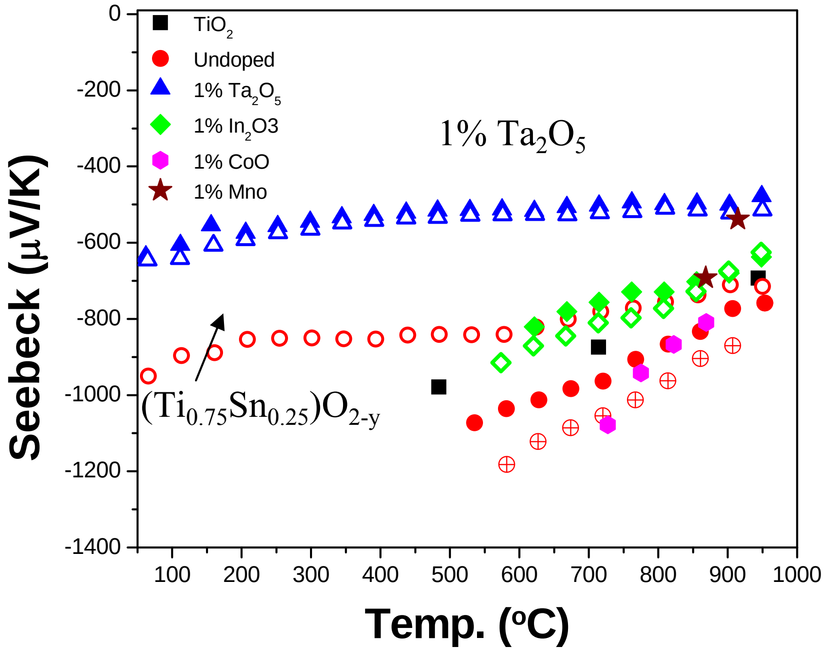
50/50 & 25/75 TiO_2/SnO_2



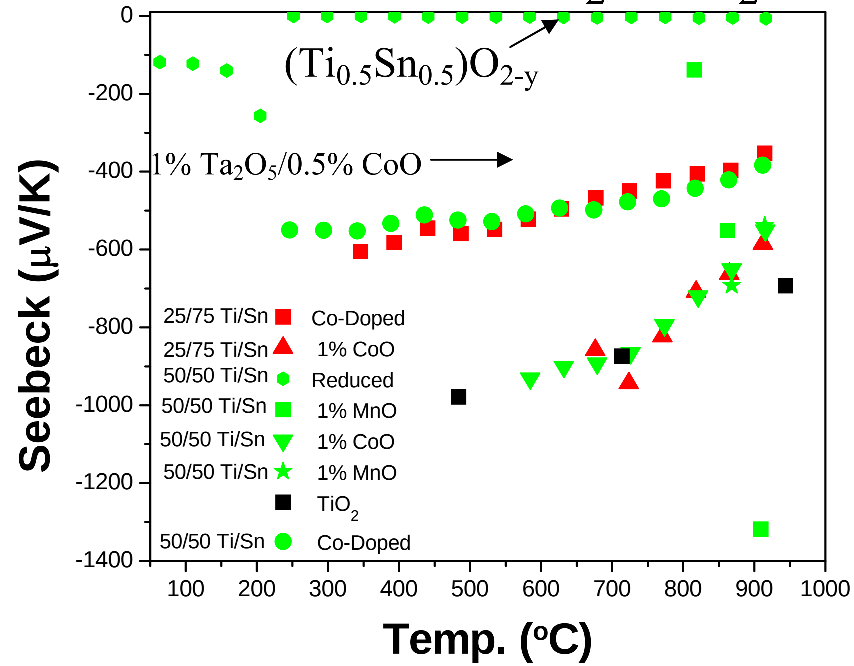
- Ta_2O_5 – Increases σ – E_a~0.25 ev
- $(Ti_xSn_{1-x})O_{2-y}$ – Oxygen Deficiency Increases σ – E_a~0.06 ev
- Co-doping-Ta_2O_5/CoO - Increases σ – E_a~0.5-0.7 ev
- In_2O_3, MnO & CoO – Ineffective in Enhancing σ – E_a~1-4.2 ev

Seebeck Coefficient

75/25 TiO_2/SnO_2

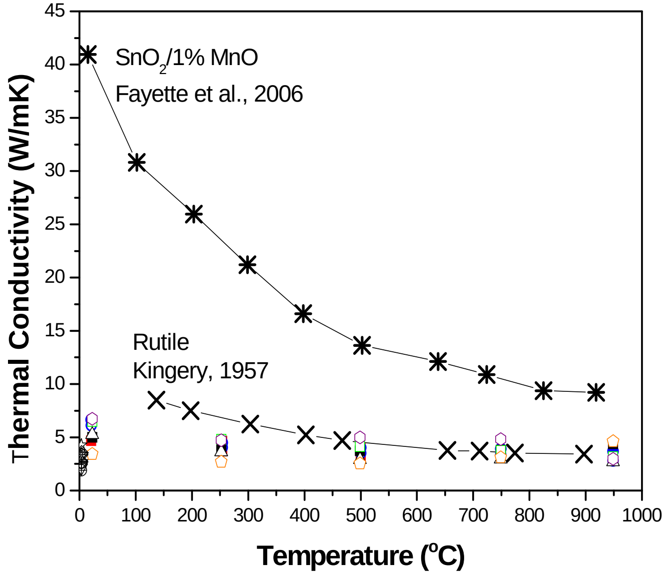


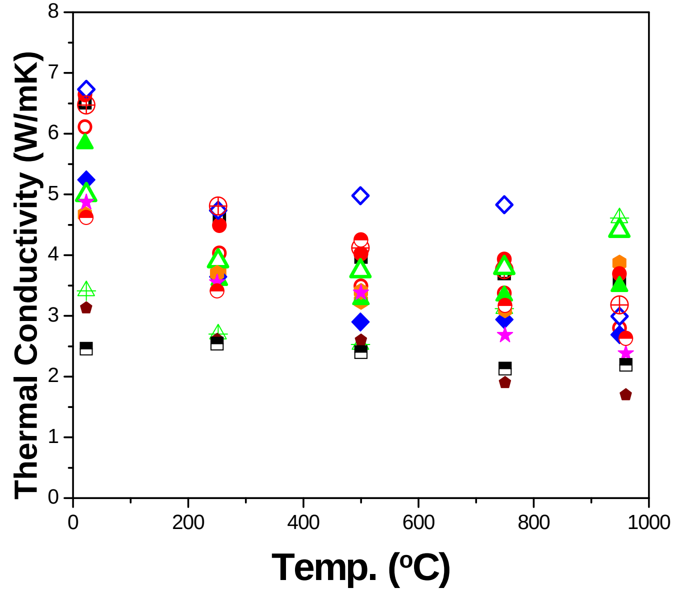
50/50 & 25/75 TiO_2/SnO_2



- N-type
- Large Seebeck coefficients >-400 μV/K
- Large Seebeck coefficient – Low σ
- $(Ti_{0.5}Sn_{0.5})O_{2-y}$ low Seebeck ~ 0

Thermal Conductivity





Compositions

1% MnO-50 TiO_2
1% CoO-50 TiO_2
1% MnO-75 TiO_2
1% CoO-75 TiO_2
1% MnO-25 TiO_2
1% CoO- 25TiO_2
1%Ta_2O_5/0.5% CoO-25 TiO_2

- Compositions exhibit low κ – 1.7 to 6.8 W/mK
- Observe no dependence on composition or post treatments
- Spinodal Decomposition – κ reduction ?
- Best ZT ~ 0.05

In Summary

•TiO_2/SnO_2 compositions exhibit low thermal conductivity. Reduction in thermal conductance by spinodal microstructure has not been isolated.

•Improvements in electrical conductivity is needed. Grain boundary phases could be detrimental. Ta_2O_5 or oxygen deficiency enhances electrical conductivity.

•Sintering aids are required to densify equal-molar and tin oxide rich compositions. MnO and CoO promoted phase separation.